Binary Alloy Phase Diagrams

Second Edition

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ments were made, the liquidus was not determined.

The Cu-Rh system is characterized by the presence of an isomorphous solid across the entire diagram in the temperature regions immediately below the solidus. The solidus determined by the incipient fusion technique appears nearly flat between approximately 25 and 50 at.% Rh. This would imply a shallow free-energy versus composition curve of the solid in corresponding composition and temperature ranges and a tendency toward formation of a miscibility gap at lower temperatures.

A single-phase continuous solid solution field exists between the components below the solidus. At still lower temperatures, the phase field enters into a wide miscibility gap wherein it separates into two equilibrium isostructural phases, one of which is rich in Cu and the other in Rh. The critical temperature and composition of the gap are 1150 °C and 60 at.% Rh, according to [71Rau].

The miscibility gap boundary given by [71Rau] has been modified slightly in this evaluation in order to include, inside the gap, the compositions for which the X-ray showed a two-phase structure. The gap boundaries at 800 °C, according to [71Rau], are approximately at 25 and 90 at.% Rh.

The existence of a metastable single-phase continuous solid solution between (Cu) and (Rh) was established by [64Luo], based on rapid solidification of the alloys from the melt. This is in agreement with the generally accepted conditions for mutual solubility of metals in the solid state, which Cu and Rh satisfy. Transition to equilibrium phases occurred when the samples were heated at 600 °C for seven to ten days.

64Luo: H.L. Luo and P. Duwez, *J. Less-Common Met.*, *6*, 248-249 (1964).

71Rau: Ch.J. Raub, E. Röschel, D. Menzel, and M. Gadhof, *Metall*, *25*(7), 761-762 (1971).

Published in *Bull. Alloy Phase Diagrams*, *2*(4), Mar 1982. Complete evaluation contains 1 figure, 2 tables, and 10 references.

Cu-Ru (Copper-Ruthenium)

P.R. Subramanian and D.E. Laughlin

Experimental data on the Cu-Ru system are very limited. Electrical resistivity measurements showed negligible solid solubility of Ru in (Cu) at 900 °C [32Lin]. There are no other reports on the Cu-Ru system.

The equilibrium phases of the assessed phase diagram are: (1) the liquid, L; (2) the fcc terminal solid solution, (Cu), with very limited solid solubility of Ru; and (3) the cph terminal solid solution, (Ru), with very limited solid solubility of Cu. The assessed diagram is schematic, because it is based on a simple thermodynamic model [83Nie].

Cu-Ru Crystal Structure Data

Phase	Composition, at.% Ru	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF4*	$Fm\bar{3}m$	*A1*	Cu
(Ru)	100	*hP2*	$P6_3/mmc$	*A3*	Mg

32Lin: J.O. Linde, *Ann. Physik.*, *15*, 219-248 (1932) in German.

83Nie: A.K. Niessen, F.R. de Boer, R. Boom, P.F. de Chatel, W.C.M. Mattens, and A.R. Miedema, *Calphad*, *7*(1), 51-70 (1983).

Submitted to the APD Program. Complete evaluation contains 1 figure, 2 tables, and 4 references.

Cu-S (Copper-Sulfur)

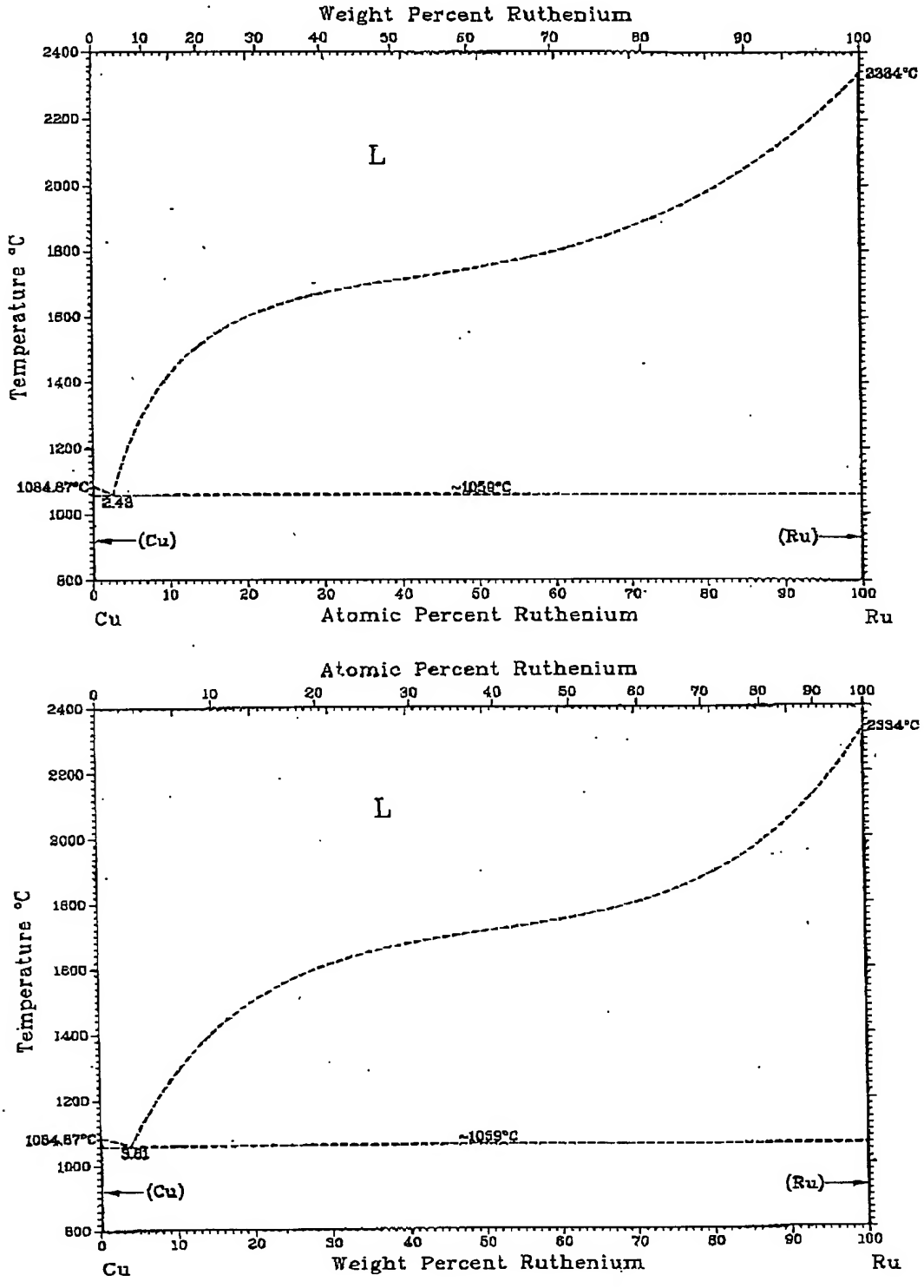
D.J. Chakrabarti and D.E. Laughlin

Numerous studies have been conducted on the Cu-S system. Uncertainty, however, persists regarding the phase equilibria, because of the strong tendency of the system to form several metastable phases. Marked thermomechanical history dependence is exhibited by many of these phases. For example, extreme sensitivity to applied pressure has been known to cause a phase transformation during specimen preparation by grinding.

However, the following features have been well established. The liquid, L,

Cu-Ru

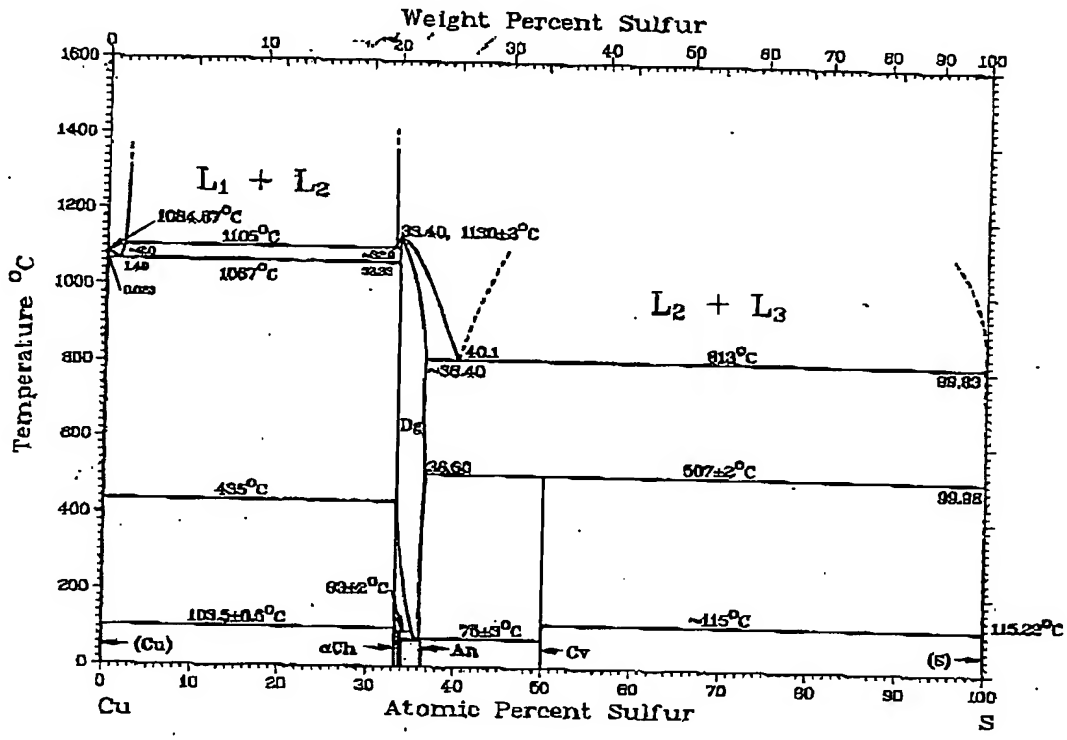
Cu-Ru Phase Diagram

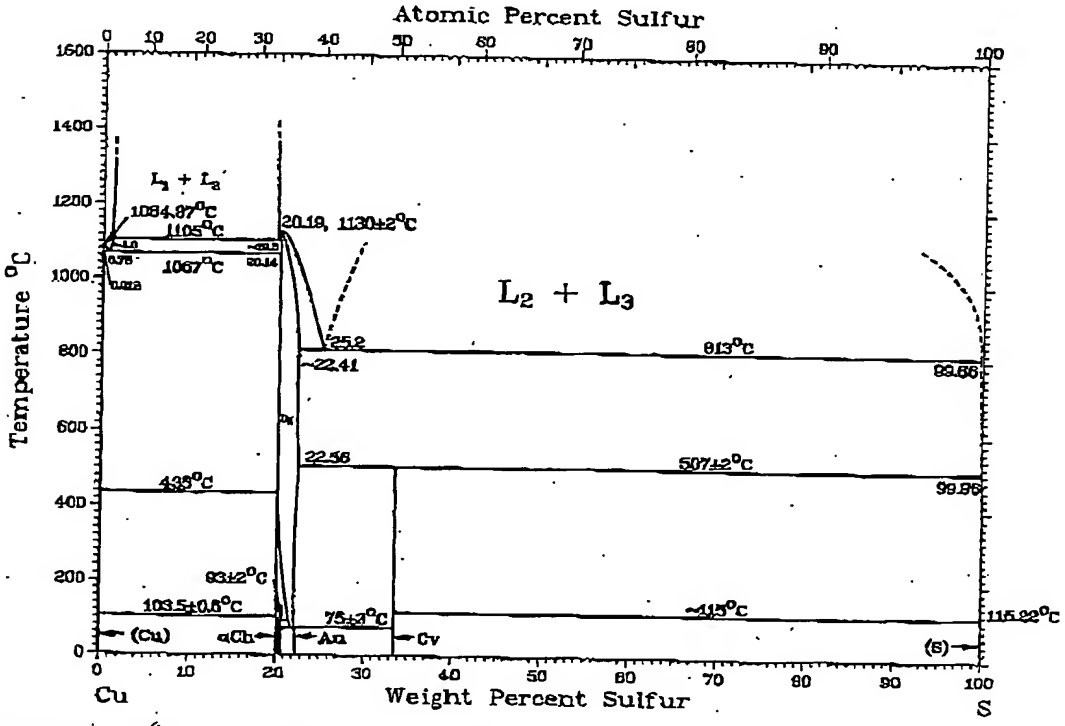


Calculated.

P.R. Subramanian and D.E. Laughlin, submitted to the APD Program.

Cu-S Phase Diagram





Compositions in parentheses are calculated values by [80Sha].

D.J. Chakrabarti and D.E. Laughlin, 1983.

Cu-S

manifests two miscibility gaps between the liquids L_1 and L_2 above 1105 °C at Cu-rich compositions and between the liquids L_2 and L_3 above 813 °C at higher S compositions. The fcc terminal solid solution, (Cu), exhibits restricted solubility of S, amounting to 0.023 at.% at 1067 °C. The solubility of S decreases with increasing purity of Cu. The orthorhombic terminal solid solution, (S), is stable up to ~115 °C, with negligible solubility of Cu.

The monoclinic low-chalcocite (αCh), is stable up to 103.5 ± 0.5 °C at the stoichiometric composition of Cu_2S and up to 90 ± 2 °C at 33.41 at.% S. The hexagonal high-chalcocite (βCh) is stable from 103.5 ± 0.5 °C at the Cu-rich limit of stoichiometric Cu_2S and from 90 ± 2 °C at 33.44 at.% S up to 435 °C at 33.34 at.% S.

The fcc digenite (Dg) has a broad phase field, with the Cu-rich boundary approximately at Cu_2S stoichiometry between 435 and 1130 ± 2 °C. The Cu-deficient boundary extends to form the defect compound $Cu_{2-\delta}S$, which is stable up to 507 ± 2 °C at 36.60 at.% S and down to 72 ± 3 °C at 35.65 at.% S.

The orthorhombic djurleite (Dj) has the nominal composition $Cu_{1.96}S$ and is stable up to 72 ± 3 °C at $Cu_{1.934}S$ and up to 93 ± 2 °C at 33.99 at.% S. The orthorhombic compound anilite (An) of stoichiometry $Cu_{1.75}S$ (36.36 at.% S) is stable up to 75 ± 3 °C. The hexagonal

Special Points of the Cu-S System

Reaction	Composition, at.% S(Cu/S)			Temperature, °C	Reaction type
L ⇌ Dg	(1.994)	33.40		1130 ± 2(a)	Congruent
L_2 ⇌ L_1 + Dg	32.9	~2.0	(2.002)	1105(b,c,d)	Monotectic
L ⇌ (Cu) + Dg	1.48	0.0225	(2.00025)		Eutectic
L_2 ⇌ Dg + L_3	40.09	~36.4	99.83	813(d,e)	Monotectic
(Cu) + βCh ⇌ αCh	~0	~33.33 ± 0.02	~33.33 ± 0.02	103.5 ± 0.5(f)	Peritectoid
βCh ⇌ αCh + Dj	33.44 ± 0.06	33.41 ± 0.02	33.78 ± 0.02	90 ± 2(f)	Eutectoid
(Cu) + Dg ⇌ βCh	~0	33.344	33.340	435(a,g)	Peritectoid
Dg ⇌ Dj + An	35.65 ± 0.09	34.08 ± 0.02	36.36 ± 0.04	72 ± 3(f)	Eutectoid
βCh + Dg ⇌ Dj	33.47 ± 0.05	35.29 ± 0.03	33.99 ± 0.02	93 ± 2(f,g)	Peritectoid
Dg + Cv ⇌ An	36.17 ± 0.02	50.00 ± 0.02	36.36 ± 0.04	75 ± 3(f)	Peritectoid
Dg + L ⇌ Cv	36.60 ± 0.07	99.98	50.00 ± 0.02	507 ± 2(a,f,g)	Peritectic
L ⇌ Cv + (S)/L + Cv ⇌ (S)	~100	50	~100	~115	Eutectic/peritectic

(a) From [72Coo]. (b) From [Hansen]. (c) From [60Joh]. (d) From [47Jen]. (e) From [74Rau]. (f) From [77Pot]. (g) From [66Ros].

Cu-S Crystal Structure Data

Phase	Composition, at.% S(Cu/S)	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	~0	*cF4*	$Fm\bar{3}m$	*A1*	Cu
α chalcocite (αCu_2S)	~33.33	*mP144(?)*	$P2_1/c$	...	...
β chalcocite (βCu_2S)	~33.3	*hP6*	$P6_3/mmc$	*B8₂*	$InNi_2$
Djurleite ($Cu_{1.96}S$)	33.7 to 34.1(a)	*oP380(?)*	$Pmnm$	...	...
			$P2_1nm$(?)		
			$Pmn2_1$		
Digenite ($Cu_{2-\delta}S$)	35.5 to 36.2(b)	*cF12*	$Fm\bar{3}m$	*C1*	CaF_2
Anilite ($Cu_{1.75}S$)	36.36 ± 0.04	*oP44(?)*	$Pnma$	...	...
Covellite (CuS)	50	*hP12*	$P6_3/mmc$	*B18*	CuS
(S)	~100	*oF128*	$Fddd$	*A16*	αS
		mP48	$P2_1/a$	...	βS
		hR6	$R\bar{3}$	...	εS
Metastable phases					
Protodjurleite	33.7 (1.97)(c)	...	...	...	...
	33.3 (1.96)(d)				
Tetragonal	33.3 (1.96)	*tP12*	$P4_32_12$	...	Ge III(HP)
Hexagonal-tetragonal Cu_xS	34.1 to 36.4 (1.93 to 1.75)	...	...	...	...
Low digenite (αDg)	35.84 to 36.15 (1.790 to 1.766)(e)	...	$R\bar{3}m$	...	...
Blaubleibender covellite I	41.7 ± 1.7 (1.4 ± 0.1)	...	...	...	...
Blaubleibender covellite II	47.7 ± 2.3 (1.1 ± 0.1)	...	...	...	...
CuS_2	66.67 (0.5)	...	$Pa3$(?)	...	...

(a) At 72 °C. (b) At 80 °C. (c) At 75 °C. (d) At 93 °C. (e) At 25 °C.

compound covellite (Cv) of stoichiometry CuS is stable up to 507 ± 2 °C.

The assessed Cu-S phase diagram is based primarily on the work of [77Pot]. Data on much of the solidus and liquidus are derived from [72Coo]. Data on the Dg and Ch boundaries are based on the studies of [66Ros] and [72Coo]. Additionally, the work of [47Jen], [57Ruh], [58Dju], [59Oud], [60Joh], [69Mor], [70Mor], [74Rau], and [80Sha] were reviewed.

47Jen: E. Jensen, *Avhandl. Norske Videnskaps-Akad. Oslo, I. Mat.-Naturw. Kl., 6*, 1-14 (1947).

57Ruh: W. Ruhl and E. Saur, *Ber. Oberhess. Ges. Naturw. Heilk. Giessen, Naturw. Abt., 28*, 35-47 (1957) in German.

58Dju: S. Djurle, *Acta Chem. Scand., 12*, 1415-1426 (1958).

59Oud: J. Oudar, *Compt. Rend., 249*, 259-261 (1959) in French.

60Joh: F. Johannsen and H. Vollmer, *Z. Erzbergbau Metallhüttenwes., 13*, 318-322 (1960) in German.

66Ros: E.H. Roseboom, Jr., *Econ. Geol., 61*, 641-672 (1966).

69Mor: N. Morimoto, *Am. Miner., 54*, 1256-1268 (1969).

70Mor: N. Morimoto and K. Koto, *Am. Miner., 55*, (1-2), 106-117 (1970).

72Coo: W.R. Cook, Jr., Nat. Bur. Stand. Spec. Pub. 364, 703-712 (1972); Ph.D. thesis, Case Western Reserve University, Cleveland, OH; Gould Labs Univ. Microfilm Order No. 72-27 (1971).

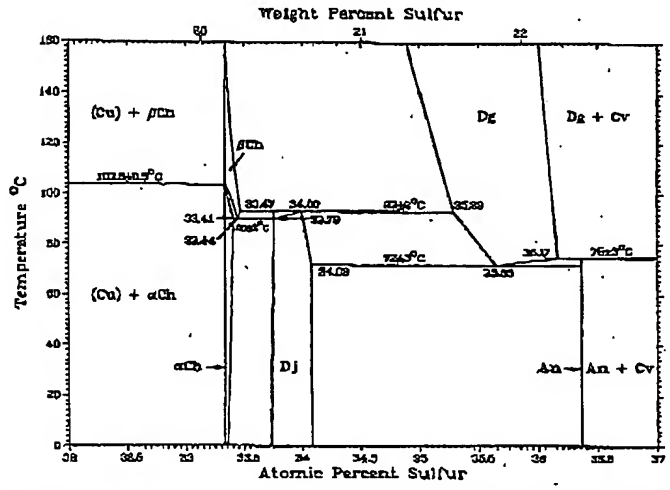
74Rau: H. Rau, *J. Phys. Chem. Solids, 35*, 1415-1424 (1974).

77Pot: R.W. Potter, II, *Econ. Geol., 72*(8), 1524-1542 (1977).

80Sha: R.C. Sharma and Y.A. Chang, *Metall. Trans. B, 11*, 575-583 (1980).

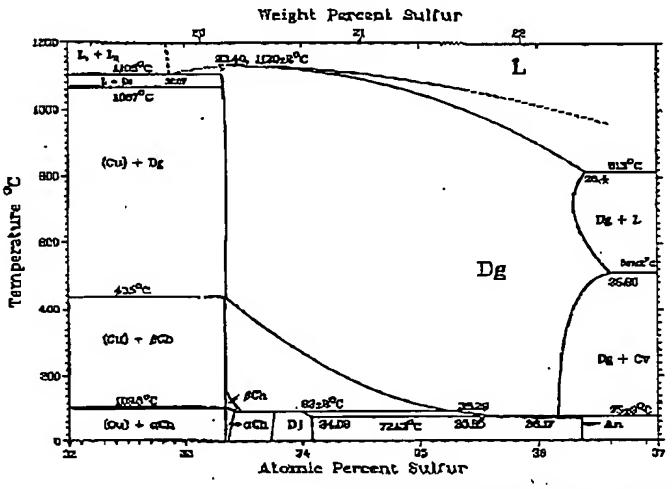
Published in *Bull. Alloy Phase Diagrams, 4*(3), Nov 1983. Complete evaluation contains 10 figures, 24 tables, and 116 references.

Enlargement of the Cu-S Diagram from 0 to 160 °C



From [77Pot]. D.J. Chakrabarti and D.E. Laughlin, 1983.

Cu-Saturated Boundary of Digenite



D.J. Chakrabarti and D.E. Laughlin, 1983.

Cu-Sb (Copper-Antimony)

Editor

The assessed Cu-Sb phase diagram is drawn essentially from [Hansen] and [Elliott], with minor modifications in the liquidus, solidus, and solvus boundaries. The liquidus is a composite of the data of [36Mur], [59Vec], [77Hay], and [83Heh], whereas the solidus of (Cu) is from [83Heh]. The solvus boundaries of (Cu) are drawn from [37Mar], [47Tar], and [58Raj]. The region between 18 and 30 at.% Sb is taken from [58Gun], and the β phase field is from [38Mur]. The solubility of Cu in (Sb) was determined to be negligible.—P.R.S.

36Mur: T. Murakami and N. Shibata, *Sci. Rep. Tohoku Imp. Univ., 25*, 527-568 (1936).

36Ela: M. Elander, G. Hagg, and A. Westgren, *Ark. Kemi Min. Geol., 12B*(1), 1 (1936).

37Mar: J.C. Martz and C.H. Mathewson, *Trans. AIME, 124*, 59-77 (1937).

38Mur: T. Murakami and N. Shibata, *Sci. Rep. Tohoku Imp. Univ., 27*, 459-484